

Determination of a Liquid State from that of Liquid Solution Coupled to it by a Common Vapor Phase

SUMMARY

We have found that NaCl solutions of different concentration and temperature, separately flowing through a chamber with a common vapor phase will be in a type of equilibrium despite the liquids not being in equilibrium with the vapor. The temperature of the liquid stream to which the vapor is flowing (the absorbing liquid) is that required to bring its calculated equilibrium vapor pressure to that of the calculated equilibrium vapor pressure of the evaporating liquid stream. We suspect this is a generally true phenomenon if the process is carried out close enough to conditions of actual equilibrium between the vapor and liquid phases.

Keywords: absorption, direct freeze concentration, equilibrium

INTRODUCTION

Cost effective absorber design often is sufficiently complicated that published models and theories are of limited use in predicting performance. This is particularly true of designs where fibrous packing is used to increase the liquid/vapor contact surface. We have found in the course of a project studying evaporatively-cooled freeze concentration that the equilibrium vapor pressure of the hygroscopic absorbent solution when it leaves the absorption section can be predicted from the temperature of composition of the solution evaporating at its triple point.

EXPERIMENTAL

In the experiments whose results are the basis of this note, sodium chloride solutions were fed to the lower section of a vigorously agitated, evacuated vessel, as shown in Fig. 1. Water evaporating from this feed cools to its

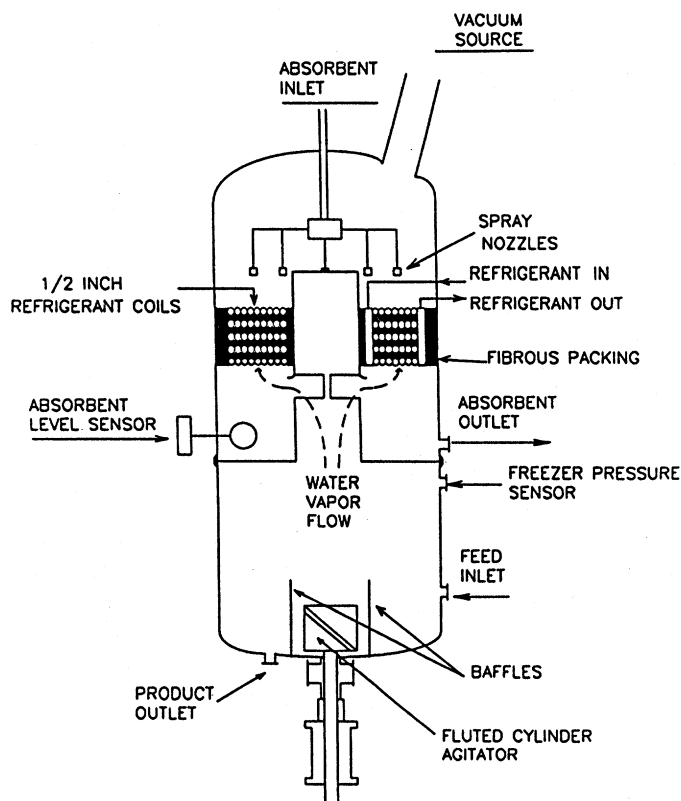


Figure 1. Freeze concentration vessel

triple point, forming ice and thereby concentrating the solute in the liquid phase. Most of the water vapor is absorbed in a solution draining through the upper section of the vessel with a smaller amount of water vapor and non-absorbed gas introduced with the feed and leaks being removed by a vacuum pump. The lower section, for the purpose of this report, is well mixed and the composition at any time represented by the exiting stream. An equilibrium vapor pressure can be calculated for the ice slurry in the lower section based on the exiting stream temperature and the triple point temperature-pressure measurements for sodium chloride solutions given by Curran (1970).

TABLE I
Measured properties of coupled NaCl solutions

Vapor pressure ^a		Temperature ^b		Absorbent Mass fraction ^c NaCl	Ice slurry Temperature ^d	
kPa	(Torr)	°C	(°F)		°C	(°F)
0.23	(1.72)	−5.9	(21.3.3)	0.228	−7.2	(19.1)
0.25	(1.91)	−4.0	(24.7)	0.222	−5.7	(21.8)
0.27	(2.01)	−3.2	(26.2)	0.199	−4.7	(23.6)
0.31	(2.34)	−1.0	(30.1)	0.228	−2.9	(26.7)
0.33	(2.51)	−0.9	(33.6)	0.225	−1.6	(29.1)
0.35	(2.62)	−0.8	(33.4)	0.213	−1.3	(29.7)
0.35	(2.61)	1.6	(34.8)	0.209	−1.6	(30.9)
0.35	(2.65)	1.9	(35.5)	0.221	−1.6	(30.9)

TABLE II
Equilibrium water vapor pressures and pressure ratio

Absorbent ^e		Ice slurry ^f		Ice ^g		100 × Δ ^h
kPa	(Torr)	kPa	(Torr)	kPa	Torr	
0.31	(2.37)	0.33	(2.50)	0.33	(2.49)	5.34
0.37	(2.77)	0.37	(2.82)	0.37	(2.84)	1.79
0.41	(3.06)	0.40	(3.10)	0.41	(3.09)	1.30
0.47	(3.52)	0.48	(3.59)	0.48	(3.60)	1.97
0.53	(3.94)	0.53	(4.00)	0.53	(4.01)	1.51
0.53	(4.00)	0.53	(4.12)	0.55	(4.11)	2.96
0.57	(4.26)	0.58	(4.36)	0.59	(4.40)	2.32
0.57	(4.27)	0.57	(4.36)	0.59	(4.40)	2.09

^a Measured with type 590 Barocel pressure sensor, Datametrix, Inc. accuracy 0.5% of reading

^b Measurement by type T thermocouple, limit of error % 1.0°C

^c Determined by correlation of refractive index, % .0005

^d Measurement by RTD, limit of error % 0.3°C

^e Calculated from Munson's equation for NaCl solutions: $\log_{10}(P) = \log_{10}(P_w) - .19986E - 2w + .137994E - 4w^2 - .48518E - 5w^3$ where P is solution vapor pressure in Torr, P_w is the pressure of pure water at the solution temperature, in Torr, w is the salt concentration in weight percent.

^f From a linear interpolation of Table I. (Curran) "Triple-point data for NaCl solutions"

^g Chemical Engineering Handbook, 6th Edition, Table 3-3, p. 3-45

^h $\Delta = 2$ (ice slurry press-absorbent pressure)/(ice slurry pressure + absorbent pressure)

In the absorption section, a concentrated solution of sodium chloride is sprayed onto a helical coil of steel tubing through which a refrigerant is circulated. The space between the tubing coils is filled with a loose packing of fibrous plastic. Concentrated absorbent drains down over the packing and coils, absorbing water vapor. Absorbent solution pools below the packing and is pumped to an evaporator. The absorbed water is removed and the regenerated absorbent is returned to the spray nozzle at the top of the absorber section. Heat for the absorbent regeneration process is provided by steam, which responds to a rise in the level of pooled absorbent keeping the absorbent concentration essentially constant during the process.

Measurements of temperature and composition (by refractive index) of the pooled absorbent solution and temperature measurements of the ice slurry, after the process had reached steady state, are shown in Table I with the measured vapor pressure. Each line of measurements was obtained for a separate run with different concentrations of feed to the freezing section.

Equilibrium water vapor pressure shown in Table II were calculated from the measurements shown in Table I. The interesting finding is that these vapor pressures of absorbent and ice slurry are close (except at the lowest pressure). As the pressures in Tables I and II show, neither liquid phase is close to equilibrium with the vapor phase. The ratio of difference of calculated equilibrium vapor pressures for the two liquid phases (absorbent/slurry) to their average is shown in the last column of Table II.

CONCLUSIONS

It is clear that at steady state the coupled liquid states must be related and that the mechanism of their interaction is based on water transfer through the vapor. Water absorption occurs in the packed section of the freeze concentration vessel and on the coiled tubing surface and evaporation from the pooled absorbent determines the absorbent composition leaving the pool for regeneration. At steady state water is evaporating from both liquid phases and the link between pressure and pooled absorbent temperature is simple. Any pooled absorbent temperature rise will increase the system pressure. This will cause a reduction of the freezing rate and water transfer rate, which finally leads to less heat of absorption and counteracts the temperature rise. If the absorbent temperature drops below that of the steady state, the reverse sequence of changes will lead to a rise in sorption rate and absorber temperature.

We could extend the statement of Chen (1988) "It is generally accepted that the vapor pressure of an aqueous solution at the freezing point must be equal to that of ice" to describe the virtual pressures of solutions which are coupled by a common vapor phase to solutions at their freezing point, virtual pressure being the equilibrium vapor pressure of a solution which is not at equilibrium. It is interesting that the vapor/liquid equilibrium

pressure can be used to identify properties of coupled liquid phases even when there is no vapor/liquid equilibrium and it might be expected that a number of kinetic features such as interfacial area and mixing with the bulk would be needed to characterize the situation.

Although the generality of this phenomenon is not established, where it is valid it permits thermodynamic data such as values of water activity, for example the work of Chen (1988) or Thurmond (1988) to be used rather than more complicated calculations based on mass transfer coefficients to design processes with coupled liquids. Also the freezing process can be monitored by pooled absorbent temperature measurement.

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